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㉒ Production of hexavalent chromium for use in chlorate cells.

㉓ By-product hypochlorite from the electrolytic production of chlorates, notably sodium chlorate, is used to form hexavalent chromium for use in the electrolysis process by oxidation of trivalent chromium compounds by the hypochlorite. The hypochlorite may be the condensate produced by treatment of the chlorate cell by-product gas stream and/or present in the cell liquor.

EP 0 266 128 A2

PRODUCTION OF HEXAVALENT CHROMIUM FOR USE IN CHLORATE CELLS

The present invention relates to the formation of hexavalent chromium useful in the electrolytic production of aqueous chlorate solutions.

An aqueous solution of sodium chlorate and sodium chloride is conventionally produced by the electrolysis of aqueous sodium chloride in diaphragmless electrolytic cells. The extent of electrolysis is controlled to produce an effluent from the cell in which the sodium chlorate and sodium chloride have the desired ratio, usually in the range (expressed as a weight ratio) of about 1:1 to about 20:1 and preferably in the range of about 2:1 to about 15:1. The aqueous solution may be further processed to crystallize out the sodium chlorate for a variety of purposes, for example, in the production of chlorine dioxide for use in the bleaching of chemical cellulosic pulps, by reduction in the presence of a strong mineral acid, usually sulphuric acid, or the aqueous solution may be used as such, for example, in the production of chlorine dioxide.

In the electrolysis of sodium chloride to form sodium chlorate, hexavalent chromium conventionally is added to the brine feed to the cell to improve significantly the current efficiency of the cell in the conversion of sodium chloride to sodium chlorate, by suppressing the reduction of hypochlorite at the cathode. Usually, sodium dichromate is employed to provide the hexavalent chromium.

The aqueous sodium chloride electrolysis produces a gaseous by-product, mainly hydrogen but also some oxygen, chlorine and steam, especially when metal anodes are employed and the electrolysis occurs at elevated temperature. The by-product gas steam is passed through a condenser wherein the steam is condensed to form an aqueous solution of hypochlorous acid, typically about 23 to 15 gpl HOCL, which also contains small amounts of dissolved chlorine. The highly corrosive nature of the condensate restricts the methods of dealing with it. For example, use in the formation of make-up liquor for chlorate production introduces severe corrosion problems. In addition if the condensates were to be reintroduced directly to the cells, water imbalances could result, which are undesirable.

Hypochlorite also usually is present in the sodium chlorate product stream from the cells as a result of inefficient chlorate formation and is removed by so-called "de-hypoing", either prior to crystallization of the sodium chlorate where the sodium chlorate is desired in that form, or prior to discharge of an aqueous solution of sodium chlorate and sodium chloride where the sodium chlorate is desired in that form. Such dehypoing is conventionally effected by heating the sodium chlorate solution at an elevated temperature for a time sufficient to remove most of the hypochlorite by conversion to chlorate and then by treatment with a reducing chemical to remove the remainder.

In accordance with the present invention hexavalent chromium useful in the electrolysis of chlorides to form chlorates is formed by reaction between a trivalent chromium compound and hypochlorite present in an effluent from the chloride electrolysis. In this way, at least part of the hypochlorite ions are converted to harmless chloride ions while providing the needed hexavalent chromium from readily-available trivalent chromium compounds.

The process of the invention can be used to effect treatment of the hypochlorous acid-containing condensate, to effect treatment of aqueous chlorate solution to achieve dehypoing, or a combination depending on the hexavalent chromium ion requirement and the amount of oxidizing agent available for oxidation. When the condensate is treated with trivalent chromium in accordance with the present invention, the resulting deactivated condensate containing only chloride ions and chromate ions, then can be used in brine preparation for the cell.

Any convenient source of trivalent chromium such as chromic chloride, chromic oxide or chromic hydroxide, may be employed in hypochlorite removal in accordance with the invention. These materials are readily available commercially, or may be provided from other sources. In one embodiment of the invention, the trivalent chromium which is used herein is trivalent chromium formed as a result of the treatment of aqueous chlorate solution to remove hexavalent chromium therefrom, as is conventionally effected when the sodium chlorate is supplied to a customer in that form.

In one preferred aspect of the latter embodiment, the process of the present invention is effected using chromic hydroxide formed in the manner described in copending U.S. patent application Serial No. 866,726 filed May 27, 1986 (E 185), assigned to the assignee hereof, the disclosure of which is incorporated herein by reference. In that application, there is described a process wherein hexavalent chromium values are removed from sodium chlorate solutions in the form of chromic hydroxide ($Cr(OH)_3$) precipitate, by reaction of the hexavalent chromium values with dithionite in the presence of critical amounts of hydroxyl ions.

The presence of that invention comprises:

(a) adding to said aqueous chlorate solution at least sufficient hydroxyl ions to provide alkaline pH conditions and an effective mole ratio of hydroxyl ions to dichromate ions of at least 3:1 so as to permit Cr(III) to form $\text{Cr}(\text{OH})_3$ as a precipitate.

5 (b) adding a dithionite to said aqueous chlorate solution to reduce Cr(VI) to Cr(III) under said alkaline pH conditions and to cause precipitation of $\text{Cr}(\text{OH})_3$, and

(c) separating the precipitate from said aqueous chlorate solution.

Preferably the addition of hydroxyl ions to said aqueous chlorate solution is in a quantity sufficient to produce a mole ratio of hydroxyl ions to dichromate ions of no more than about 6.1 and most preferably is in a quantity sufficient to produce a mole ratio of hydroxyl ions to dichromate ions of from about 3:1 to

10 about 5.1. The said addition of a dithionite to said aqueous chlorate solution is preferably in a quantity sufficient to provide a mole ratio of $\text{S}_2\text{O}_4^{2-} : \text{Cr}_2\text{O}_7^{2-}$ of at least about 3.0:1

The hexavalent chromium-forming reaction effected in this invention is best achieved in basic solution, although an acidic solution may be employed. For the removal of hypochlorite from off-gas condensate by the process of the invention, therefore, it is preferred to add at least sufficient sodium hydroxide or other 15 convenient alkalinizing agent to the condensate prior to contact with the trivalent chromium.

The present invention is particularly directed to the formation of hexavalent chromium for use in the electrolytic production of aqueous sodium chlorate from aqueous sodium chloride. However, the present invention may also be used for the formation of hexavalent chromium for use in the electrolytic production of any aqueous chlorate solution by the electrolysis of the corresponding chloride and in which the 20 hexavalent chromium is useful. Such aqueous chlorate solutions include aqueous solutions of alkali metal chlorates. Such as sodium chlorate, potassium chlorate, lithium chlorate, rubidium chlorate and cesium chlorate, alkaline earth metal chlorates, such as beryllium chlorate, magnesium chlorate, calcium chlorate, strontium chlorate, barium chlorate and radium chlorate, and mixtures of two or more such chlorates, which may also contain dissolved quantities of alkali metal chlorides, alkaline earth metal chlorides and mixtures 25 thereof.

Electrolytically-produced sodium chlorate solution usually contains dissolved quantities of sodium chloride and this solution is generally termed "cell liquor". The concentration of sodium chlorate and of sodium chloride in cell liquor may vary widely, depending on the extent of electrolysis of the sodium chloride solution. Generally, the concentration of sodium chlorate may vary from about 100 to about 750 30 gpl, preferably about 250 to about 675 gpl, and the concentration of sodium chloride may vary from about 20 to about 400 gpl, preferably about 50 to about 300 gpl. Typically, cell liquor contains about 600 gpl of sodium chlorate and about 100 gpl of sodium chloride.

The concentration of hexavalent chromium which is required in the electrolysis process depends on the particular product being formed. For the production of cell liquor, hexavalent chromium usually is added to 35 the electrolyte in an amount sufficient to provide a hexavalent chromium concentration in the range of about 0.1 to about 20.0 grams of dichromate ions per litre of solution, preferably about 0.2 to about 10.0 gpl, typically about 2 gpl.

Although the hexavalent chromium is usually added to the aqueous chloride electrolyte solution in the form of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), other forms of water-soluble hexavalent chromium may be employed, for example, sodium chromate (Na_2CrO_4), potassium chromate (K_2CrO_4) and mixtures of two or 40 more of such materials may be employed.

Where the hexavalent chromium is present in the chlorate solution other than as dichromate ions, for example, as CrO_4^{2-} , the mole ratio of $\text{OH}^- : \text{Cr}_2\text{O}_7^{2-}$ upon addition of hydroxide ions is determined on a chromium equivalent basis.

45 The sole Figure of the drawing is a schematic flow sheet of sodium chlorate plant modified in accordance with one embodiment of this invention.

Referring to the drawing, sodium chloride solution is fed by line 10 to chlorate cells 12 wherein the sodium chloride solution is electrolyzed in cells connected in series or in parallel to form an aqueous sodium chlorate solution, also containing unreacted sodium chloride, which is removed from the chlorate 50 cells 12 as a product stream by line 14. The electrolytic cells 12 effect diaphragmless electrolysis of the sodium chloride between electrodes. The anodes are preferably metal anodes, so that the electrolysis can be run at elevated temperatures, which increases the reaction rate and the concentration of sodium chlorate which can be present in the cell liquor.

Such metal anodes, also termed "dimensionally stable anodes", are well known in the electrolytic art, and comprise a substrate, formed of titanium, zirconium, tantalum or hafnium, with an electroconductive coating of a precious metal, for example, platinum; a precious metal alloy, for example, a platinum-iridium alloy; a metal oxide, for example, ruthenium or titanium oxide; mixtures of two or more of such materials; or 5 a platinate, for example, lithium platinate or calcium platinate. The cells may be operated generally at a temperature of about 40° to 120°C, preferably about 70°C to about 90°C when using such metal anodes.

The electrolysis process produces hydrogen as a by-product. The elevated temperature of operation of the cell also produces steam and some chlorine gas is resulting off-gas stream is forwarded by line 16 to a condenser 18 wherein the off-gas stream is cooled, generally to a temperature of about 10° to about 70°C, 10 preferably about 30° to about 60°C, to condense the stream. As a result of dissolution of the gaseous chlorine present in the off-gas stream in the condensed stream, the resulting condensate contains hypochlorous acid and dissolved chlorine. Generally, the concentration of hypochlorous acid is about 2 to about 15 gpl HOCL, particularly about 6 to about 8 gpl HOCL, and the concentration of dissolved chlorine is about 0.01 to about 5 gpl Cl₂, particularly about 0.1 to about 1 gpl Cl₂.

15 The gas stream resulting from the condenser 18 is passed by line 20 to a chlorine scrubber 22 wherein residual quantities of contaminating gases, usually chlorine, are removed by scrubbing in one or more operations, typically with alkali or brine, in a scrubber 22, leaving a purified hydrogen stream for discharge by line 24. Any oxygen present in the off-gas stream 16 is discharged with the hydrogen stream 24.

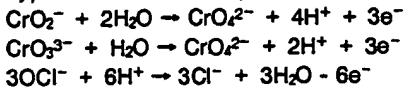
20 The cell liquor in line 14 contains dissolved hypochlorite as a result of incomplete formation of chlorate from electrolysis products and usually this hypochlorite is removed in a dehypo tank 26. The concentration of hypochlorite present in the cell liquor in line 14 generally is about 1 to about 5 gpl and preferably about 1.5 to about 3.5 gpl.

25 The dehypod cell liquor is forwarded in the illustrated embodiment by line 28 to a crystallizer 30, wherein sodium chlorate is crystallized from the cell liquor and solid sodium chlorate is recovered as the product by line 32. Mother liquor from the crystallization of the sodium chlorate is recycled by line 34 to a brine preparation system 36, wherein the sodium chloride solution feed in line 10 is prepared.

30 The condensate from the condenser 18, as noted previously, has a relatively high concentration of hypochlorous acid and is highly corrosive. This condensate represents a difficult disposal problem in a conventional sodium chlorate plant which utilizes metal electrodes and an elevated temperature cell operation. In accordance with the present invention, the condensate is passed by line 38 to a treatment tank 40 wherein the condensate is contacted with a trivalent chromium compound, for example, chromic hydroxide or chromic chloride, fed by line 42 to the treatment tank 40. The trivalent chromium compound is oxidized by the hypochlorite ions and the chlorine to useful hexavalent chromium compound while the hypochlorite ions and chlorine are reduced to harmless chloride.

35 The process may be effected over a wide range of pH but is most effective at pH values of about 6 to about 14, preferably about 8 to about 10. These pH conditions facilitate dissolution of the chromium (III) and oxidative conversion to chromium (VI). Accordingly, it is preferred to add sodium hydroxide or other suitable alkali to the condensate prior to reaction with the trivalent chromium compound..

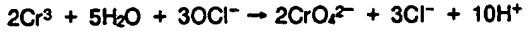
Under alkaline pH conditions, chromium (III) dissolved as chromite (CrO₂²⁻ and CrO₃³⁻) and the 40 hypochlorite can be depicted as follows:



45 The overall reaction can be repeated as follows.

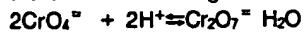
$$2\text{CrO}_2^{2-} + \text{H}_2\text{O} + 3\text{OCl}^- \rightarrow 2\text{CrO}_4^{2-} + 3\text{Cl}^- + 2\text{H}^+$$

Under acidic conditions, the corresponding overall reaction may be represented as follows:



50 Accordingly, two moles of Cr³⁺ reduce three moles of OCl⁻ to produce two moles of Cr^{VI}. The hydrogen ions which are formed are neutralized when the process is carried out under alkaline conditions by the alkalinity of the reaction medium.

Although the above equations depict the hexavalent chromium as being formed as chromate, usually the chromate undergoes further reaction to form dichromate as follows:



55 The reaction of Cr^{VI} with the condensate in the treatment tank 40 produces a solution containing chloride ions and hexavalent chromium and depleted with respect to the hypochlorite, which then can be forwarded by line 44 to the brine preparation tank 36. The hexavalent chromium is beneficial to the electrolysis reaction in the cells 12 and is conveniently added, as discussed earlier.

The present invention, therefore, provides a means of providing the hexavalent chromium requirements of the cell while treating the condensate stream. The extent to which the hypochlorite present in the condensate can be treated using the process of the invention depends on the extent to which the hexavalent chromium that results can be employed in the chlorate plant or elsewhere.

5 In the brine preparation tank 36, the feed of sodium chloride for the cells 12 in line 10 is prepared from the recycle mother liquor in line 34, the hexavalent chromium-and chloride-containing solution in line 44 and solid sodium chloride in line 48.

Trivalent chromium also may be used to effect dehyping in the tank 36 to remove hypochlorite and again form hexavalent chromium and chloride ions. The hexavalent chromium ions so produced are 10 recycled to the brine preparation tank 36 with the mother liquor 34.

The dehyping of the cell liquor in the tank 26 may be effected in combination with treatment of condensate in tank 40. The extent to which both procedures can be employed is limited by the extent to which the resulting hexavalent chromium can be employed in the electrolysis process, or otherwise.

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EXAMPLES

This Example illustrates the use of chromium hydroxide to treat hypochlorite solution.

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Example 1

Chromic hydroxide solids were removed from cell liquor as a precipitate following the procedure described in Example 1 of U.S. Serial No. 866,726 (Case E185), as follows:

25 100 ml of synthetic cell liquor containing 550 gpl NaClO₃, 100 gpl NaCl and 3 gpl Na₂Cr₂O₇.2H₂O was treated with 3 ml of 1 M NaOH (mole ratio NaOH:Na₂Cr₂O₇ = 3:1) at 25°C. The resulting precipitate was removed by centrifugation.

30 A series of experiments was conducted in which the aqueous solution containing precipitated chromic hydroxide so formed was heated to the desired temperature, the required amount of a 10% aqueous solution of sodium hydroxide was added to establish the desired pH and sodium hypochlorite solution in the form of chlorate cell off-gas condensate then was added to oxidize the precipitate to the soluble hexavalent form.

The results of the series of experiments are summarized in the following Table I.

35

Table I

| TEST | TEMP (°C) | INITIAL | pH | OXIDATION END TIME (MIN) | NaOCl:Cr | NaOH:Cr | % oxidized (3:2) |
|------|--------------|---------|------|-----------------------------|------------|------------|------------------------|
| | | | | | mole ratio | mole ratio | |
| 40 | 1 | 22 | 7.1 | 4.0 | 60 | 4:2 | 0:1 |
| | 2 | 40 | 7.1 | 3.8 | 30 | 4:2 | 0:1 |
| | 3 | 65 | 7.1 | 3.7 | 30 | 4:2 | 0:1 |
| 45 | 4 | 23 | 11.7 | 9.5 | 20 | 7:2 | 3:1 |
| | 5 | 45 | 11.7 | 9.7 | 10 | 7:2 | 3:1 |
| | 6 | 24 | 11.0 | 7.3 | 30 | 5:2 | 1:1 |
| 50 | 7 | 24 | 11.5 | 9.3 | 30 | 5:2 | 2.5:1 |
| | 8 | 25 | 11.7 | 10.1 | 45 | 6:2 | 5:1 |

55 As may be seen from the results set forth in Table I, the process of chromic hydroxide oxidation at ambient temperature was relatively slow and higher temperatures and initial alkaline pH increased the oxidation yield and decreased the oxidation time.

Example 2

This Example illustrates the use of chromic chloride to treat hypochlorite solution.

5 A further series of experiments were conducted in which the chlorate cell off-gas condensate was treated with 1 M NaOH solution to establish the desired pH and chromic chloride solution 0.3309 M was gradually added thereto at ambient temperature. The chromic chloride was added in batches and, after each chromic chloride addition batch, the pH was readjusted with 1 M NaOH solution to the initial pH and the oxidation-reduction potential (ORP) of the solution was measured. Chromic chloride addition was repeated until a significant drop in ORP had occurred, significantly removal of hypochlorite.

10 The results of this further series of experiments are set forth in the following Table II:

Table II

| TEST | HOCl (g/L) | pH | END ORP (mV) | HOCl:Cr mole ratio 3:2) | NaOH:Cr mole ratio |
|------|---------------|-----|-----------------|-------------------------------|-----------------------|
| 1 | 6.3 | 7.2 | 915 | 2.4:2 | 8.6:1 |
| 2 | 9.9 | 7.5 | 845 | 2.5:2 | 6.2:1 |
| 20 | 3 13.8 | 7.5 | 850 | 3.5:2 | 7.4:1 |
| | 4 2.2 | 9.0 | - | 5:2 | - |

25 As may be seen from the results of Table II, the reaction of the chromic chloride with hypochlorite was almost stoichiometric.

In summary of this disclosure, the present invention provides a novel manner of providing hexavalent 30 chromium for use in the electrolytic production of chlorates which uses by-product hypochlorite from the chlorate production to oxidize trivalent chromium to hexavalent chromium. Modifications are possible within the scope of this invention.

Claims

35 1. A process for the electrolytic production of a chlorate by the diaphragmless electrolysis of an aqueous solution of the corresponding chloride in the presence of a hexavalent chromium ions wherein at least one product stream from the electrolysis process contains hypochlorite ions characterised in that hexavalent chromium ions are formed by reaction between the hypochlorite in said at least one product stream and trivalent chromium ions and the hexavalent chromium ions are utilized in the electrolysis process.

40 2. A process according to claim 1, characterised in that said trivalent chromium ions are provided by a chromic compound selected from the group consisting of chromic chloride, chromic oxide and chromic hydroxide.

45 3. A process according to either of claims 1 or 2, characterised in that the product stream from the said electrolysis which comprises hypochlorite ions is the aqueous chlorate product stream.

4. A process according to claim 3, characterised in that said aqueous chlorate product stream contains about 1 to about 5 gpl of hypochlorite.

5. A process according to claim 4, characterised in that said aqueous chlorate product stream contains about 1.5 to about 3.5 gpl of hypochlorite.

50 6. A process according to any of the preceding claims, characterised in that said trivalent chromium ions are formed as a result of the treatment of an aqueous chlorate solution to remove hexavalent chromium therefrom.

7. A process according to any of the preceding claims, characterised in that said reaction between 55 hypochlorite and trivalent chromium ions is affected at a pH greater than 6.

8. A process according to claim 1, characterised in that the electrolytic production of sodium chlorate is carried out at an elevated temperature and forms a hydrogen off-gas stream also containing steam and chlorine gas, said hydrogen off-gas stream is treated to provide an effluent hydrogen stream substantially

free from contaminants and an aqueous condensate containing condensed steam, hypochlorite and dissolved chlorine, and hexavalent chromium ions are formed by reaction between hypochlorite in said condensate and trivalent chromium ions.

9. A process according to claim 8, characterised in that electrolysis is effected at a temperature of about 60° to about 120°.

10. A process according to claim 9, characterised in that said electrolysis is effected at a temperature of about 70° to about 90°.

11. A process according to any of claims 8 to 10, characterised in that said treatment of said hydrogen off-gas stream includes condensing said steam by cooling said off-gas stream to a temperature of about

10 10° to about 70°, thereby to form a condensate containing about 2 to about 15 gpl HOCl.

12. A process according to claim 11, characterised in that said treatment of said hydrogen off-gas stream includes condensing said steam by cooling said off-gas stream to a temperature of about 30° to about 60°, thereby to form a condensate containing about 6 to about 8 gpl HOCl.

13. A process according to any of claims 8 to 12, characterised in that said trivalent chromium ions are provided by a chromic compound selected from the group consisting of a chromic chloride, chromic oxide and chromic hydroxide.

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